ESR Spectrum and Magnetic Behavior of Copper(II) Sebacate

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The magnetic susceptibility of copper(II) sebacate, measured between 5 and 400 K, confirms the presence of strongly coupled Cu-Cu pairs. The ESR spectrum, obtained with a polycrystalline sample, shows an important rhombic anisotropy and supports a $d_{x^2-y^2}$ ground-state.

Key words: Copper(II) sebacate; ESR spectrum; Magnetic behavior.

Introduction

Different attempts have been made to correct the abnormalities related to Menkes' disease, an inherited disorder associated with problems in copper absorption [1–3]. Copper supplementation has attained great interest not only in relation with this and other physiological disorders [4, 5] but also in veterinary medicine [6]. The copper(II) complex of sebacic acid (decanedioic acid) appears as a very promising system in this context.

In recent papers we described a method for the facile synthesis of this complex, complemented with spectroscopic studies, solubility tests and lipophilicity assays [7, 8].

In order to advance in a more complete characterization of this interesting compound, we have investigated its magnetic behavior through magnetic susceptibility measurements and ESR spectroscopy.

1. Experimental

Copper(II) sebacate, CuC$_{10}$H$_{16}$O$_4$, was obtained by treating sodium sebacate with copper(II) sulfate, following the procedure described in [7]. It was characterized by chemical analysis and infrared spectroscopy [7, 8].

Magnetic susceptibility measurements were performed between 5 and 400 K using a Quantum Design SQUID magnetometer employing a magnetic field of 1 kG.

The ESR spectra were recorded at 100 and 300 K with a Bruker-300 spectrometer using 34.01 GHz (Q-band). The frequency of the cavity was determined with a Hewlett-Packard 5352 B microwave frequency counter, and the magnetic fields by means of a Bruker NMR, model ER035 Gaussmeter.

2. Results and Discussion

Our previous studies of the complex demonstrate the existence of a dimeric structure containing Cu-Cu moieties, bridged by carboxylate groups [7], similar to that found in the well known copper(II) acetate and other Cu(II) complexes of carboxylic acids [9–11].

The plot of the magnetic susceptibility as a function of temperature, shown in Fig. 1, is characteristic for strongly coupled dimeric copper units. It shows a broad maximum at approximately 260 K and a clear trend to diminish at lower temperatures, an usual behavior in discrete antiferromagnetically ordered systems. Below 30 K, the susceptibility increases, probably due to the presence of a small paramagnetic impurity.

The observed magnetic behavior can be described by an equation derived by Bleaney and Bowers [12], based on the Heisenberg isotropic spin Hamiltonian,

$$ H = - 2 J S_1 S_2, $$

for two coupled $S = 1/2$ systems, and introducing an additional term which accounts for the...
The ESR spectrum registered in the Q-band and shown in Fig. 2 is characteristic for a triplet $S = 1$ state with appreciable zero-field splitting, which probably arises from the combined effects of the anisotropic and antisymmetric exchange and from the classical dipole-dipole interaction. The spectrum could be interpreted with the spin Hamiltonian

$$H_{ss} = \beta H g S + D (S_z^2 - 2/3) + E (S_x^2 - S_y^2),$$

where $D = 3/2 D_z$ and $E = 1/2 (D_x - D_y)$ are the parameters related to the zero-field splitting of the triplet state. In a system with rhombic symmetry, and for randomly oriented samples, six spin allowed transitions ($\Delta M_s = \pm 1$) may be observed if $h \nu > D > 3 E$. The magnetic fields at which these transitions can be observed ($H_{X1}, H_{X2}, H_{Y1}, H_{Y2}, H_{Z1}, H_{Z2}$) were determined by Waserman et al. [13], giving six equations depending on the microwave frequency and the eigenvalues of the $g$ and $D$ tensors. This method has the restriction that both tensors have the same principal axes.

Besides these allowed transitions, there are two forbidden ones ($\Delta M_s = \pm 2$), which are frequently observed [14]. One of them ($H_{MIN}$) corresponds to the absorption of one photon, which induces a transition between the levels $M_s = -1$ and $M_s = +1$. The other one ($H_{DO}$), corresponds to the absorption of two quanta, which generate the same transition [14].

Therefore one obtains a self-consistent set of eight equations which can be solved by repeated interaction in order to obtain the parameters of interest, namely $g_x, g_y, g_z, D$ and $E$. Adjusting the observed signals by means of a least squares refinement to the respective equations, the following values were obtained:

$$g_x = 2.069, \quad g_y = 2.043, \quad g_z = 2.321,$$

$$D = 0.338 \text{ cm}^{-1}, \quad E = -0.012 \text{ cm}^{-1}.$$

The marks in Fig. 2 indicate the calculated positions of the transition. This analysis does not allow to obtain the real signs of $D$ and $E$ and shows only the relative values of one with respect to the other. Notwithstanding, they are important in the assignment of the observed transitions, specially in cases such as the present one, in which the anisotropy of the $g$ tensor is important.

Although a clear rhombic anisotropy is evident, all the obtained parameters are of the same order as that which the maximum of the susceptibility is observed, $T (\chi_{max}) = 1.2 J/k = 260 \text{ K}$, 217 K is obtained for $J/k$, confirming the validity of the used model.

The dependence of the molar magnetic susceptibility of copper(II) sebacate on temperature is shown in Fig. 1. The best fit of experimental data is attained with the following parameters:

$$J/k = -220 \text{ K} \quad (153 \text{ cm}^{-1}), \quad g = 2.11, \quad q = 0.04.$$

The paramagnetic contribution:

$$X = (1 - q) \frac{N g^2 \beta^2}{k T} \left[ \frac{1}{1 + \exp(-2 J/k T)} \right] + q \frac{N g^2 \beta^2}{4 k T},$$

where all terms have their usual meaning and $q$ is the percentage of the paramagnetic impurity.

The value obtained for $J$ is totally reasonable for our system. Taking into account the temperature at
usually observed in classic Cu(II) dimers [14–16], but the use of the Q-band in the measurements shows an evident rhombic anisotropy that is often lost when the experiments were carried out with the X-band.

On the other hand, and as the lowest g-value is higher than 2.04, one can deduce that $d_{x^2-y^2}$ must be the ground state of Cu(II) in this complex. Therefore, the environment of the metal center may be an elongated octahedron or a distorted square based pyramid [17].

The spectrum of Fig. 2 also shows a signal corresponding to an uncoupled Cu(II) impurity, probably the same which gives rise to the paramagnetic contribution observed at low temperatures in the susceptibility measurements. This signal is probably due to the presence of the monomeric species resulting from breaks of the Cu-Cu dimers.

To conclude, this study allowed to obtain a good insight into the magnetic behavior of copper(II) sebacate, confirming the existence of a pair of strongly coupled Cu-Cu dimers and a significant rhombic distortion of the coordination sphere around the metal centers.

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